



(11) **EP 1 390 984 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
26.08.2009 Bulletin 2009/35

(21) Application number: **02769351.4**

(22) Date of filing: **07.05.2002**

(51) Int Cl.:
H01L 29/788 ^(2006.01) **H01L 29/51** ^(2006.01)

(86) International application number:
PCT/US2002/014237

(87) International publication number:
WO 2002/091476 (14.11.2002 Gazette 2002/46)

(54) **FLOATING GATE MEMORY DEVICE USING COMPOSITE MOLECULAR MATERIAL**

FLOATING-GATE-SPEICHERBAUSTEIN, DER ZUSAMMENGESETZTES MOLEKULARMATERIAL
VERWENDET

DISPOSITIF DE MEMOIRE A GRILLE FLOTTANTE UTILISANT UNE MATIERE MOLECULAIRE
COMPOSITE

(84) Designated Contracting States:
DE GB

(30) Priority: **07.05.2001 US 289091 P**

(43) Date of publication of application:
25.02.2004 Bulletin 2004/09

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(56) References cited:
EP-A- 0 727 822

- **PATENT ABSTRACTS OF JAPAN** vol. 1995, no. 07, 31 August 1995 (1995-08-31) -& JP 07 106440 A (HITACHI LTD), 21 April 1995 (1995-04-21)
- **KRIEGER Y H: "STRUCTURAL INSTABILITY OF ONE-DIMENSIONAL SYSTEMS AS A PHYSICAL PRINCIPLE UNDERLYING THE FUNCTIONING OF MOLECULAR ELECTRONIC DEVICES" JOURNAL OF STRUCTURAL CHEMISTRY, PLENUM PRESS, NEW YORK, NY, US, vol. 4, no. 40, 1999, pages 594-619, XP008005141 ISSN: 0022-4766 cited in the application**
- **R.KURITA ET AL.: "Field modulation effects on charge-density-wave conduction in NbSe3" PHYSICA B. CONDENSED MATTER., vol. 284-288, 2000, pages 1661-1662, XP002212806 AMSTERDAM., NL ISSN: 0921-4526**

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Description**FIELD OF THE INVENTION**

[0001] The invention relates to a floating gate memory cell for data storage applications, and more particularly, to a floating gate memory device having a variable resistance dielectric as a gate insulator.

BACKGROUND OF THE INVENTION

[0002] Computer data storage, in particular random access memory (RAM) has become an increasingly important component of electronic hardware. There are various distinct types of memory devices, distinguished by their speed and data retention characteristic. Dynamic random access memory (DRAM) is a volatile memory characterized by a destructive read. This means that it is necessary to supply voltage to the memory bits at all times, or the information will disappear. Furthermore, each memory element has associated with it a transistor. Static random access memory (SRAM) stores data in a bistable flip-flop, commonly consisting of cross-coupled inverters. It is called "static" because it will retain a value as long as power is supplied. It is still volatile, i.e. it will lose its contents when the power is switched off, in contrast to ROM. SRAM is usually faster than DRAM, but each bit requires several transistors (about six), so that a lesser number of bits of SRAM fit in the same area as compared to DRAM.

[0003] When the gate electrode of a conventional MOSFET is modified so that semi-permanent charge storage inside the gate is possible, the new structure becomes a nonvolatile memory device (floating gate transistor). Nonvolatile memory devices have been extensively used in integrated circuits, such as the electrically alterable read-only memory (EAOM), the erasable-programmable read-only memory (PROM), and the nonvolatile random-access memory (NVRAM).

[0004] In a floating gate transistor, charges are injected from the silicon across a first insulator and stored in the floating gate or at the insulator-oxide interface. The stored charge gives rise to a threshold voltage shift, and the device is at a higher-threshold voltage state. A long retention time is required for nonvolatile memory operation. The retention time is defined as a time when the stored charge decreases to 50% of its initial value. For a well designed memory device, the charge retention time can be over 100 years. To erase the stored charge and return the device to a "low-threshold voltage state," a high reverse voltage is applied to the gate and/or the device is exposed to UV light. The conventional erase process is relatively slow.

EP 0 727 822 discloses a memory apparatus on a semiconductor substrate including first and second electrodes, wherein a resistance value between the first and second electrodes are arranged to advantageously change from a high to a low resistance state.

[0005] There is a need for a floating gate memory device with decreased erase time and that does not require the application of LTV light.

SUMMARY OF THE INVENTION

[0006] These and other needs are met by embodiments of the present invention which provide a floating gate memory device comprising a substrate and a first insulating layer on the substrate. A floating gate is provided on the first insulating layer, and a second insulating layer is on the floating gate. A control gate is formed on the second insulating layer. At least one of the first or the second insulating layers has a controllably variable resistivity wherein the resistivity can be changed in response to the application of an electric field to switch the resistivity from a highly resistive state, where charge is retained by the floating gate, to a lower resistivity state, where the charge stored on the floating gate can be drained off to the control gate and wherein the resistivity can be restored to the highly resistive state in response to the application of an electric field of reverse polarity.

[0007] In certain embodiments, at least one of the first and second insulating layers consists of a molecular matrix with ionic complexes distributed through the molecular matrix and wherein the ionic complexes are dissociable in the molecular matrix under the influence of an applied electronic field.

[0008] The earlier stated need are also met by further aspects of the invention wherein at least one of the first and second insulating layers comprises a material switchable between low and high conductivity states in response to an applied electric field, and wherein the material is a molecular matrix with ionic complexes distributed in the molecular matrix, the ionic complexes being dissociable in the molecular matrix under the influence of an applied electric field.

[0009] The foregoing and other features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Fig. 1 shows a nonvolatile memory device that is a floating gate transistor constructed in accordance with an embodiment of the present invention;

[0011] Fig. 2a-d show a molecular composite material between two electrodes in various operational states according to a current theoretical understanding of the invention;

[0012] Fig. 3 shows a voltage-current characteristic for write and erase operations of the memory device of the present invention; and

[0013] Fig. 4 shows the dependence on writing pulse critical amplitude on writing pulse time.

DETAILED DESCRIPTION OF THE INVENTION

[0014] Referring first to Fig. 1, a floating gate transistor may be considered to be a modified MOSFET transistor with a floating conductive pad embedded in the dielectric that insulates the gate from the source/drain. Because of the very high resistivity of commonly used dielectrics, such as SiO_2 and Si_3O_4 , any electric charge deposited on the floating gate will remain there during the retention time of the device, which can be years. However, it is difficult to discharge the floating gate simply by applying a reverse external electric field because of the large electrical resistance of the tunnel barrier in the reverse direction. For this reason, the conductivity of the dielectric is typically enhanced by illuminating the dielectric with UV light. The present invention provides a structure that avoids the need for UV light.

[0015] The present invention address and solves problems related to the control and structure of a floating gate memory device. In particular, the present invention provides for a floating gate memory device that has an insulating layer that acts to either electrically insulate the floating gate from a control gate, or has an increased conductivity to allow for a rapid discharge of the floating gate charge. This is achieved, in part, by employing a floating gate transistor having an insulating layer between the control gate and the floating gate that comprises a composite material that exhibits structural electronic instability in one dimension and enables static and dynamic control over the conductivity of the composite material. As an exemplary composite material, a molecular matrix is employed with ionic complexes in the matrix. Under the application of an electric field, the ionic complexes dissociate controllably to change the electrical conductivity of the insulating layer.

[0016] Figure 1 depicts an exemplary embodiment of the floating gate memory device constructed in accordance with present invention. The floating gate memory device includes substrate 12 in which are formed source and drain regions 14, 16, respectively.

[0017] A first insulator 18 is formed on the substrate 10 and spans the source and drain regions 14, 16. A floating gate 20 formed of conductive material, is formed on the first insulating layer 18. A second insulating layer 22 is formed on the floating gate 20, followed by the formation of gate electrode 24 on the second insulating layer 22. The gate electrode 24 and the drain region 16 are depicted as being connected to voltages V_g and V_d , respectively. The gate electrode 24, like the floating gate 20, comprises a conductive material.

[0018] According to certain embodiments, at least one of the two dielectric layers 18, 22 depicted in Fig. 1 comprise a one-dimensional molecular system exhibiting a transition from a low electrical conductivity to a high electrical conductivity and *vice versa*. This transition is typically manifested by an S-shaped (reentrant) voltage-current characteristic with metastable or stable memory. The impedance of such memory cells can be between ~ 10

M Ω and $\sim 100 \Omega$ for example, depending on the switching condition. Examples of such molecular systems are systems with a low dimensionality exhibiting a so-called Peierls transition.

5 **[0019]** A number of different materials may be used as the insulating layers 18, 22. Exemplary materials are described in more detail below, but are also discussed in an article by Yu H. Krieger, entitled "Structural Instability of One-Dimensional Systems as a Physical Principle Underlying the Functioning of Molecular Electronic Devices", Journal of Structural Chemistry, Vol. 40, No. 4, 1999 (Yu H. Krieger), expressly incorporated by reference herein.

10 **[0020]** There are two predominant types of structural organization of such systems. First, there are strands of linear conjugated polymers, which are weakly bonded to each other and whose mutual arrangement is generally poorly organized. Second, there are crystal structures, where the individual molecules form one-dimensional columns and interact with each other much more actively than molecules from different columns do.

15 **[0021]** Polyconjugated systems primarily involve polyvinylenes, i.e., polymers with an acyclic conjugation system, in which the one-dimensional character of structure is dictated by the mechanism of conjugation in linear macromolecules. Polyacetylene is a classical representative of this class of polymers. Its electronic structure is a prototype for many other conjugated polymers.

20 **[0022]** Another wide class of molecular compounds are formed from aromatic and heterocyclic molecules which possess high electric conductivity due to π -bonds between molecules. Such molecular systems are called π -complexes or charge transfer complexes, with those systems whose structure involves isolated one-dimensional columns or strands possessing pronounced electro-physical properties of interest for switching and memory applications. Molecular charge transfer complexes are donor-acceptor systems formed from two molecules: one possessing donor and another acceptor properties.

30 Among the well-defined complexes with a one-dimensional structure, tetra-cyano-quino-dimethane (TCNQ) are planar molecules with unsaturated bonds, arranged in a crystal as parallel stacks forming a quasi-one-dimensional system.

35 **[0023]** In another class of one-dimensional systems, the cations are dynamically disordered. It involves molecular compounds having the general formula $(\text{TMTSF})_2\text{X}$. Transition metal salts of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\text{X} \cdot 3\text{H}_2\text{O}$ (KCP) type are also the typical representatives of mixed-valence quasi-one-dimensional complexes, as are phthalocyanines and porphyrins. Moreover, pure inorganic compounds, such as NbSe_3 , are also interesting examples of compounds with quasi-one-dimensional structure.

40 **[0024]** While not being bound by theory, the following is currently believed by the inventors to describe the mechanism for the conductivity change in the material in the present invention. An exemplary molecular compos-

ite that can be applied as at least one of the insulating layers 18, 22 in the floating gate transistor 10 is shown in Figs. 2a - 2d. The molecular composite includes a quasi-one-dimensional, or at least structurally and electrically anisotropic, molecular matrix, wherein ionic complexes are distributed in the matrix. Polyconjugated compounds, such as the exemplary quasi-one-dimensional systems described above, for example, polyphenylacetylene, can be used as the anisotropic molecular matrix. The ionic complex can be a salt, such as sodium chloride (NaCl), or any other material that can dissociate in an applied electric field. The exemplary anisotropic molecular matrix is depicted in Figs. 2 a-d as comprising an assembly of chain-like molecules oriented perpendicular to the electrode surfaces. However, other orientations of those molecules or of anisotropic "channels" are possible as long as a charge separation of the type depicted in Figs. 2 a-d is enabled.

[0025] Electric switching in the molecular thin films depicted in Figs. 2a-d is characterized by the existence of two stable states, a high impedance state ("off" state) and a low impedance state ("on" state). The impedance of this "off" state is usually more than $\sim 10\text{ M}\Omega$, for example. Switching from the "off" state to the "on" state occurs when an applied electric field exceeds a threshold value. The impedance of this "on" state can be less than $\sim 100\ \Omega$, for example. A transition from "on" state back to the "off" state can take place by reversing the polarity of the electric field.

[0026] Two modes of the "on" state are identifiable: a metastable mode (Fig.2b) and a stable mode (Fig.2c). The metastable mode of the memory cell function is characterized by the low P_W and P_{ER} value (0.1-0.5V), high impedance of the "ON" state (wide region, about $1\text{ k}\Omega$ - $1\text{ M}\Omega$), short switching time (less than $1\ \mu\text{s}$), and short retention time between about 10 s or several hours. Conversely, the stable mode of the memory cell operation shows the high P_W and P_{ER} value (3-10V), low impedance of the "ON" state (less than $100\ \Omega$), long switching time (1 ms and more) and long storage time (between several months and years). Some memory cells made from this material have been observed to exhibit substantially unchanged electrical properties in the stable mode after storage for six years.

[0027] Fig. 2a illustrates the "off" state, where the electrical conductivity is essentially zero, assuming that the anisotropic molecular matrix itself is a good electrical insulator. When an external electric field E is applied, as indicated in Fig. 2b, the sodium salt dissociates into sodium and chlorine ions, and the ions are displaced from their original position in the anisotropic molecular matrix, resulting in an increase in the electrical conductivity to the metastable "on" state. Upon further increase of the electric field, the ions become more strongly separated (Fig. 2c), accompanied by a still further increase in the conductivity of the "on" state to the above-described stable state. When a very large field is applied over a long time, the anions and cations accumulate at the electrodes

(Fig. 2d), resulting in a sharp decrease in the electrical conductivity due to the absence of mobile charges ("off" state).

[0028] The electrode material can be, for example, a metal, such as Al or Cu, ITO, a semiconductor or a conducting polymer. The transition from the "off" state depicted in Fig. 2a to the "on" state depicted in Fig. 2b requires application of an external voltage of approximately 3-5 V for a time period of approximately 10-100 ns. The transition from the "off" state depicted in Fig. 2a to the "on" state depicted in Fig. 2c having a higher electrical conductivity and longer retention time is achieved by applying an external voltage of approximately 3-5 V for a time period of approximately 300 ns - $1\ \mu\text{s}$. A molecular composite comprising polyphenylacetylene and -5-7% NaCl as the ionic complex are described in these figures as an exemplary embodiment

[0029] In an application as a variable conductivity gate insulator with a floating gate transistor, replacing at least one of the traditional dielectrics (e.g., insulating layer 22), the conductivity is switched between a low conductivity state, where charge is retained by the floating gate, and a higher conductivity state, where the charge stored on the floating gate 20 can be drained off to the gate electrode 24. The floating gate 20 can thereafter be restored to its original state, i.e., isolated from the gate 24, by applying a reverse potential between the source/drain 14, 16 and the gate electrode 24.

[0030] The current-voltage (I-V) characteristic of a floating gate transistor, as it applies to the state of the composite material forming, for example, insulating layer 22, is shown in Fig. 3. The positive voltage applied to the gate electrode with respect to the ground will be referred to as write voltage (in pulsed experiments, as write pulse) (P_W), which renders the insulating layer 22 conductive, and the negative voltage, which restores the insulating properties of insulating layer 22, as erase voltage (or erase pulse) (P_{ER}), respectively.

[0031] Fig. 3 shows a typical I-V curve for write (positive applied voltage) and erase operation (negative applied voltage). The device is in the "off" state, until the applied voltage reaches a critical value of approximately 0.3 V. In the "off" state, the electric current through the memory cell is essentially zero. When the applied voltage exceeds the critical voltage of 0.3V, the memory cell 10 approaches zero resistance, with the voltage across the cell dropping to a very small value and the current increasing to more than $120\ \mu\text{A}$, with the cell attaining the "on" state. The cell remains in the "on" state until a negative voltage is applied, which in the present example is approximately -1 V. This represents the erase cycle: After the erase cycle is completed, the cell is again in the "off" state. The parameter (voltage, pulse duration) used for the erase operation depend on the characteristic values of the "on" state of the device.

[0032] Referring now to Fig. 4, the pulse duration of a write pulse required to change the conductivity of the insulating layer 22 is related to the amplitude of the write

pulse. For example, insulating layer 22 may be switched from the "off" state to the "on" state by applying a pulse of 4 V for 10 μ s, whereas a pulse duration of more than 1 ms may be required when writing with a voltage of approximately 1 V. Accordingly, the speed with which the conductivity of the insulating layer 22 of the device 10 changes can be adapted to specific applications.

[0033] The present invention thus provides an easily erasable floating gate transistor memory chip for systems, employing molecular memory cells. The electronic circuitry of the erasable floating gate transistor memory chip can be based on that of well-developed DRAM chips. Depending on the "state" of the memory cell, i.e., a metastable or stable state, the circuit can work as either SRAM or DRAM.

Claims

1. A floating gate memory device, comprising:

a substrate (10);
a first insulating layer (18) on the substrate (10);
a floating gate (20) on the first insulating layer (18);
a second insulating layer (22) on the floating gate (20); and
a control gate (24) on the second insulating layer (22);
wherein at least one of the first (18) and second insulating (22) layers has as controllably variable resistivity which can be changed in response to the application of an electric field to switch the resistivity from a highly resistive state, where charge is retained by the floating gate, to a lower resistivity state, where the charge stored on the floating gate can be drained off to the control gate and wherein the resistivity can be restored to the highly resistive state in response to the application of an electric field of reverse polarity.

2. The device of claim 1, wherein at least one of the first (18) and second (22) insulating layers comprises a molecular matrix, wherein the at least one of the first (18) and second (22) insulating layers further comprises ionic complexes distributed through the molecular matrix and wherein the ionic complexes are dissociable in the molecular matrix under the influence of an applied electric field.

3. The device of claim 2, wherein the molecular matrix comprises a polyconjugated compound, and wherein the polyconjugated compound is one of polyparaphenylene, polyphenylvenylene, polyaniline, polythiophene, or polypyrrole.

4. The device of claim 2, wherein the molecular matrix comprises one selected from aromatic and hetero-

cyclic molecules,
a quasi-one-dimensional complex,
an anisotropic inorganic material,
a molecular compound of (TMTSF)₂X,
a transition metal salt of K₂Pt(CN)₄Br_{0.3}·3H₂O (KCP) type.

Patentansprüche

1. Speicherbauelement mit Gate mit einstellbarem Potential, mit:

einem Substrat (10);
einer ersten isolierenden Schicht (18) auf dem Substrat (10);
einem Gate mit frei einstellbarem Potential (20) auf der ersten isolierenden Schicht (18);
einer zweiten isolierenden Schicht (22) auf dem Gate mit frei einstellbarem Potential (20); und
einem Steuergate (24) auf der zweiten isolierenden Schicht (22);
wobei die erste isolierende Schicht (18) und/oder die zweite isolierende Schicht (22) einen steuerbar variablen Widerstand besitzt, der sich in Reaktion auf das Anlegen eines elektrischen Feldes ändert, um den Widerstand von einem Zustand mit hohem Widerstandswert, in welchem Ladung in dem Gate mit frei einstellbarem Potential gehalten wird, in einen Zustand mit geringem Widerstandswert umzuschalten, in welchem die in dem Gate mit frei einstellbarem Potential gespeicherte Ladung an das Steuergate abgeführt wird und wobei der Zustand mit hohem Widerstandswert in Reaktion auf das Anlegen eines elektrischen Feldes mit umgekehrter Polarität wieder hergestellt werden kann.

2. Bauelement nach Anspruch 1, wobei die erste isolierende Schicht (18) und/oder die zweite isolierende Schicht (22) eine molekulare Matrix aufweist, wobei die erste isolierende Schicht (18) und/oder die zweite isolierende Schicht (22) ferner ionische Komplexe enthält, die in der molekularen Matrix verteilt sind und wobei die ionischen Komplexe unter dem Einfluss eines angelegten elektrischen Feldes in der molekularen Matrix dissoziierbar sind.

3. Bauelement nach Anspruch 2, wobei die molekulare Matrix eine polykonjugierte Verbindung aufweist und wobei die polykonjugierte Verbindung eine der folgenden ist: Polyparaphenylene, Polyphenylvenylene, Polyanilin, Polythiophen oder Polypyrrol.

4. Bauelement nach Anspruch 2, wobei die molekulare Matrix eines der folgenden Bestandteile aufweist: ein aromatisches Molekül, ein heterozyklisches Molekül,

einen quasi-eindimensionalen Komplex,
 ein anisotropes organisches Material,
 eine Molekularverbindung aus $(\text{TMTSF})_2\text{X}$,
 ein Übergangsmetallsalz der Art K_2Pt
 $(\text{CN})_4\text{Br}_{0,3}\times 3\text{H}_2\text{O}$ (KCP).

$\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0,3}\times 3\text{H}_2\text{O}$ (KCP) .

5

Revendications

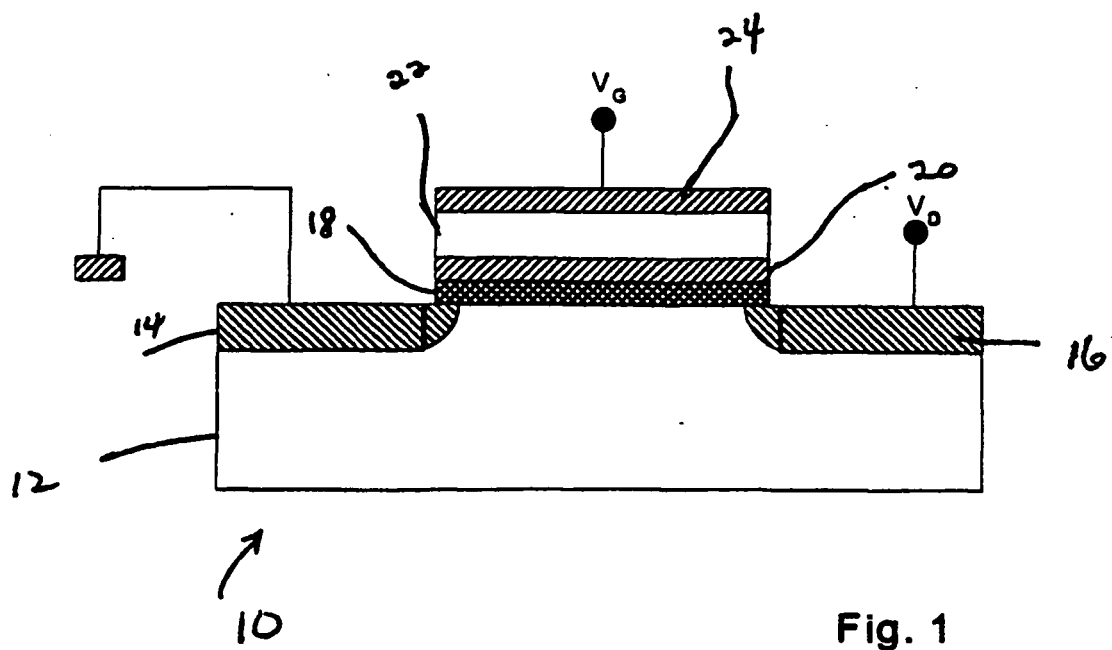
1. Dispositif de mémoire à grille flottante, comprenant : 10

un substrat (10) ;
 une première couche isolante (18) sur le substrat (10) ;
 une grille flottante (20) sur la première couche isolante (18) ; 15
 une seconde couche isolante (22) sur la grille flottante (20) ; et
 une grille de commande (24) sur la seconde couche isolante (22) ; 20
 dans lequel au moins l'une des première (18) et seconde (22) couches isolantes présente une résistivité variable de façon à pouvoir être commandée, laquelle peut être modifiée en réponse à l'application d'un champ électrique afin de commuter la résistivité à partir d'un état résistif haut, où la charge est retenue par la grille flottante, à un état résistif inférieur, où la charge stockée sur la grille flottante peut être évacuée hors de la grille de commande et dans lequel la résistivité peut être restaurée à l'état résistif haut en réponse à l'application d'un champ électrique de polarité inverse. 25 30

2. Dispositif selon la revendication 1, dans lequel au moins l'une des première (18) et seconde (22) couches isolantes comporte une matrice moléculaire, dans lequel l'une au moins des première (18) et seconde (22) couches isolantes comporte, de plus, des complexes ioniques répartis à travers la matrice moléculaire et dans lequel les complexes ioniques sont dissociables de la matrice moléculaire sous l'influence d'un champ électrique appliqué. 35 40

3. Dispositif selon la revendication 2, dans lequel la matrice moléculaire comprend un composé polyconjugué, et dans lequel le composé polyconjugué est l'un du polyparaphénylène, polyphénylvényène, polyaniline, polythiophène, ou polypyrrole. 45 50

4. Dispositif selon la revendication 2, dans lequel la matrice moléculaire comprend une molécule sélectionnée parmi des molécules aromatiques et hétérocycliques, un complexe quai-unidimensionnel, 55 un matériau anisotrope inorganique, un composé moléculaire de $(\text{TMTSF})_2\text{X}$, un sel d'un métal de transition du type



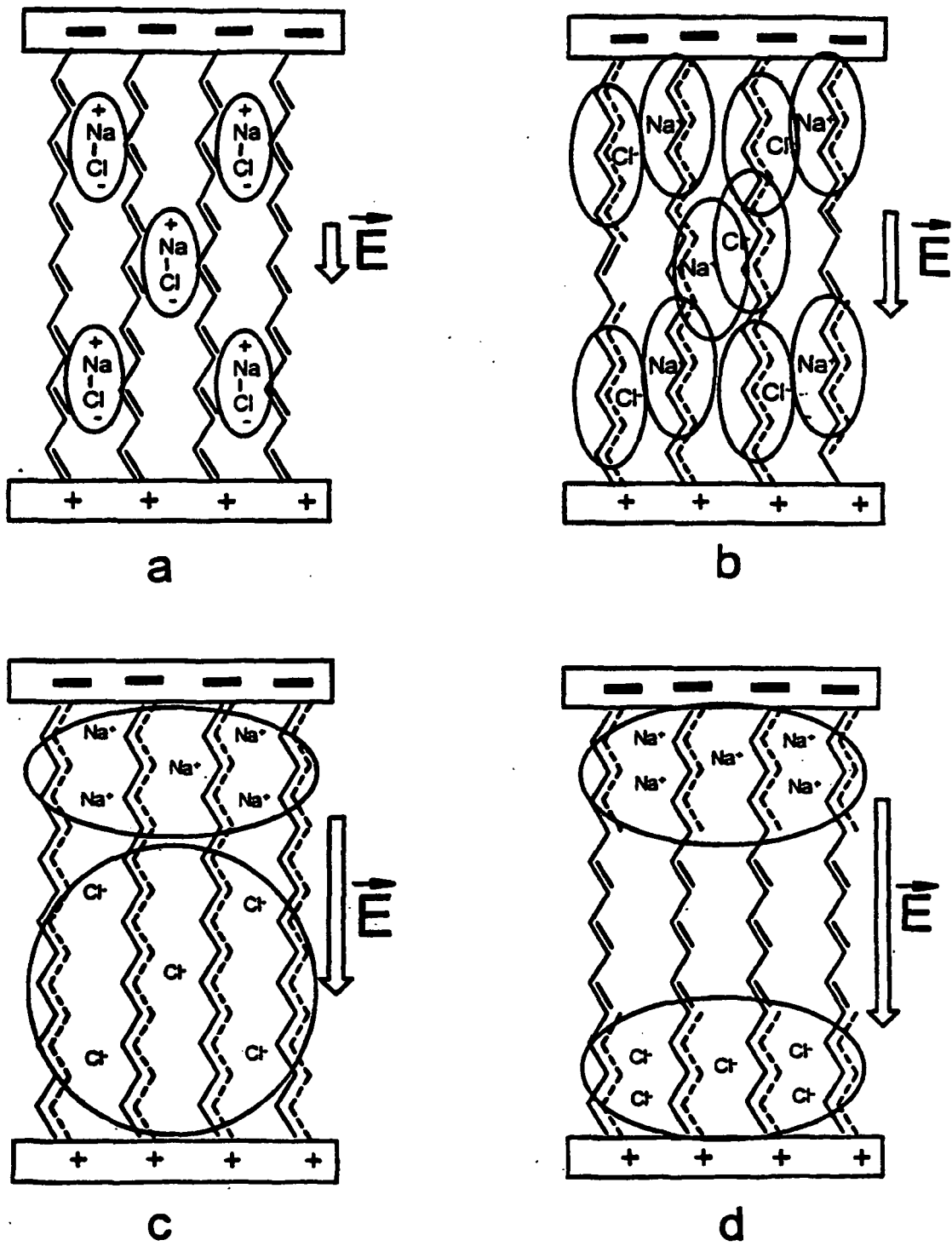


Fig.2

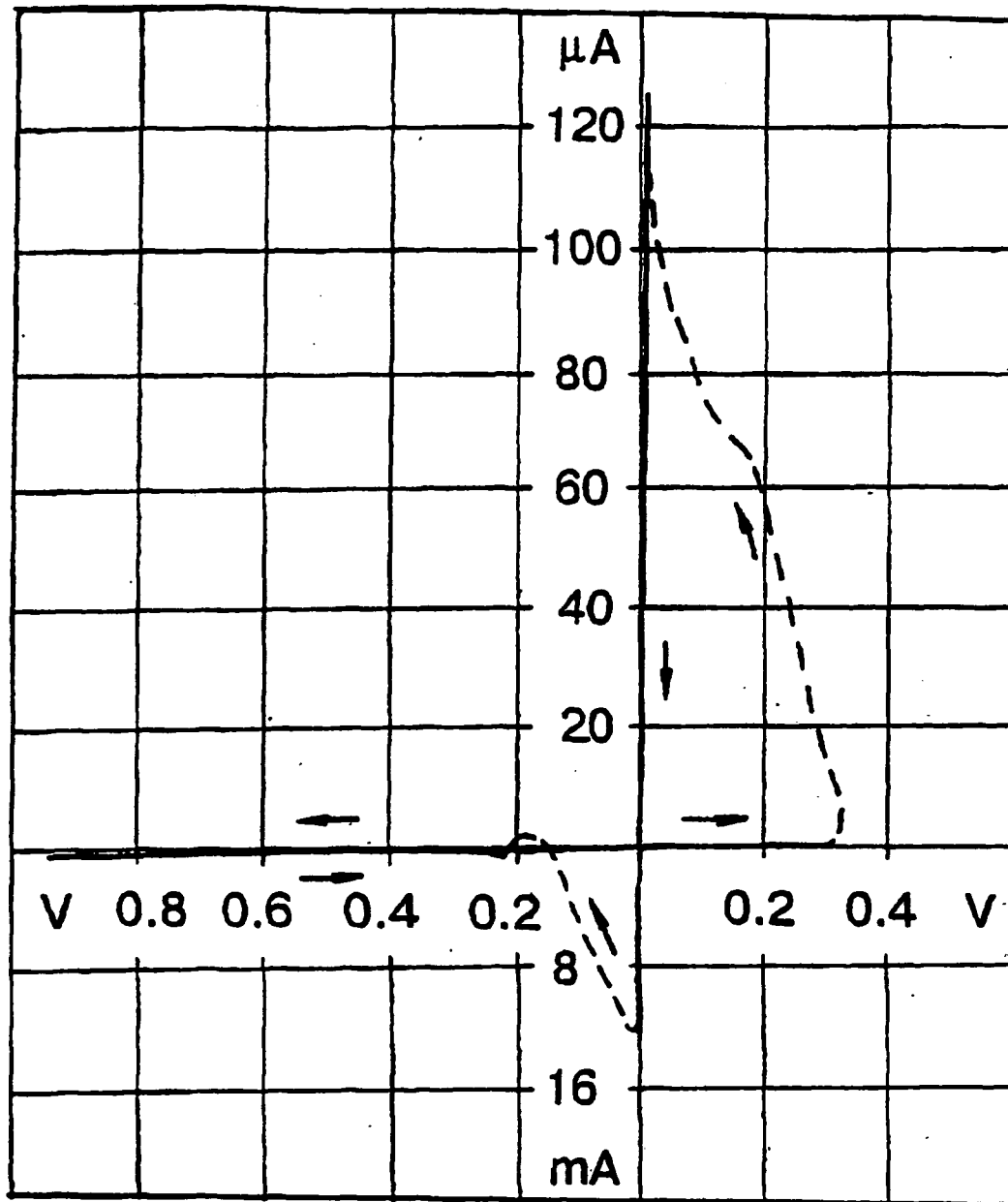
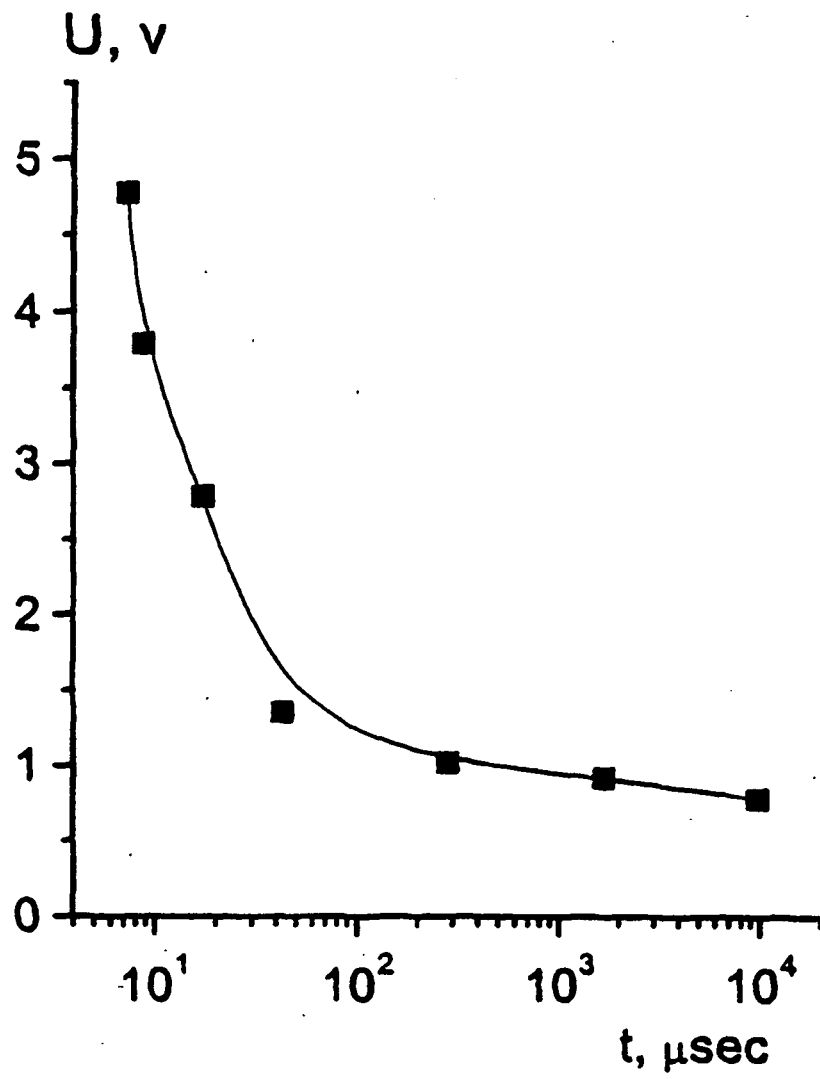


Fig. 3

 $\overline{t_{r5.4}}$

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 0727822 A [0004]

Non-patent literature cited in the description

- **Yu H. Krieger.** Structural Instability of One-Dimensional Systems as a Physical Principle Underlying the Functioning of Molecular Electronic Devices. *Journal of Structural Chemistry*, 1999, vol. 40 (4) [0019]